Effects of Backbone and Endgroup on the Decomposition Mechanisms of PFPE Lubricants and their Tribological Performance at the Head-Disk Interface

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Abstract

Tribo-chemical studies of the lubricant endgroup effect on the tribology of the head/disk interface (HDI) were conducted using carbon disks coated with PFPE lubricant. The studies involved drag tests with uncoated and carbon-coated Al_2O_3-TiC sliders in an ultra-high vacuum (UHV) tribochamber. The UHV drag tests show that a good lubricant should have one active OH endgroup and one non-active endgroup. The active one insures the lubricant is adsorbed very well onto the disk carbon surface, resulting in a lower removal rate of the lubricants during the contact sliding. The non-active one prevents the catalytic decomposition of the lubricant in the presence of the Al_2O_3 surface of the uncoated slider. The studies also demonstrate that the catalytic degradation process of ZDOL in the presence of Lewis acid occurs most readily at the acetal units (-O-CF_2-O) within the internal backbones (CF_2O and CF_2CF_2O) instead of the endgroup functionals. Therefore, Demnum, without any acetal units, experiences less catalytic degradation with the uncoated Al_2O_3/TiC sliders as compared to ZDOL.

Keywords: Tribochemistry; PFPE, Hydrogenated carbon overcoat; Decomposition; Friction and wear; Endgroup, Backbone, Lewis acid, Acetal.

I. Introduction

To reduce friction and wear, magnetic recording thin-film disks have a hard overcoat lubricated with a thin layer of a liquid lubricant. Because of the superior properties, such as low vapor pressure, good viscosity, high thermal stability and chemical inertness, perflouropolyethers (PFPEs) have been extensively used as the lubricants of magnetic media in hard disk drives. The molecular structure, containing only carbon, fluorine and oxygen atoms, gives PFPEs this set of properties. The PFPE lubricant and the hard carbon overcoat on the disks provide the necessary protection of the underlying magnetic film against wear due to contact sliding at the head-disk interface. Their decomposition mechanisms associated with contact sliding have been extensively studied [1-5]. Our earlier studies of the decomposition of ZDOL lubricant on nitrogenated carbon overcoats (CNx) [6] indicate that the decomposition rate is significantly affected by the slider materials. The use of uncoated Al_2O_3-TiC sliders leads to the rapid decomposition of ZDOL due to catalytic reactions, while carbon coated sliders produce less intense decomposition which are due primarily to frictional actions [7]. The thermal stability of PFPE has also been studied extensively [8-12]. In our previous report [13], the friction and catalytic decomposition mechanisms as well as the thermal behavior of ZDOL are described, and data demonstrating the chemical reactions of the lubricant and carbon overcoat are also presented.

We observed that in the presence of an Al_2O_3 surface the catalytic reactions occur at the endgroup functionals, where the fluorine atom transfer is from the endgroup to the internal sector [14]. In this report we study the backbone effect on the catalytic reactions. However, the studies demonstrate that the catalytic degradation process of ZDOL in the presence of Lewis acid occurs most readily at acetal units (-O-CF_2-O) within the internal backbones (CF_2O and CF_2CF_2O) instead of the endgroup functionals. Thus, Demnum, with no acetal units, performs less catalytic degradation with the uncoated Al_2O_3/TiC sliders as compared to ZDOL.

II. EXPERIMENTAL PROCEDURE AND SET-UP

The UHV tribochamber consists of a disk spindle, a slider actuator, a substrate heater, and a high-resolution quadrupole mass spectrometer (QMS) in a vacuum chamber with base pressure $< 2 \times 10^{-8}$ Torr, which was described in details in a previous paper [15]. The QMS provides *in-situ* detection of the gaseous products generated during drag tests and thermal desorption studies. The QMS can monitor simultaneously 15 different atomic mass units (AMUs) ranging from 1 to 500 along with friction from strain gauge transducers. It is noted that all AMUs from 1 to 192 of ZDOL decomposition products generated at the Al_2O_3/TiC slider/CHx disk interface were previously investigated under the same test conditions and only the most pertinent AMUs were monitored in this study.

Drag tests in the tribochamber were conducted as follows. Initially, the tribochamber was baked out at 150°C at high vacuum for 24 hours. The chamber was then backfilled with Argon gas as the disk and slider samples were mounted inside. Next, the chamber was pumped down to a base pressure of 2×10^{-8} Torr and the channels of the QMS were assigned to selected AMUs. Background intensities were recorded before the drag tests were initiated with the following parameters: 0.2 m/s drag speed, a load of 25 mN, and a sliding time of 20 minutes. The sliders were 30% (1.2mm by 1mm) negative-pressure Al_2O_3/TiC sliders with and without amorphous carbon films on the air bearing surfaces. The disks were commercial 95mm thin film disks with a 105Å amorphous carbon overcoat. The disks were lubricated by a dipping process. The resulting thickness of lubricant on the disks in this study was 12Å. Three different PFPE lubricants were tested, and the representation formulas of such PFPE's are as follows:

ZDOL 4200

$HO\text{-}CH_2\text{-}CF_2O\text{-}(CF_2O)m\text{-}(CF_2CF_2O)n\text{-}CF_2\text{-}CH_2\text{-}OH$, where $n/m = 2/3$

Demnum SA 5500

$CF_3\text{-}(CF_2CF_2CF_2O)m\text{-}\ CF_2\text{-}CF_2\text{-}CH_2\text{-}OH$

AM 3001

$P\text{-}\ CH_2OCH_2\text{-}CF_2\text{-}(CF_2O)_m\text{-}(CF_2CF_2O)_n\text{-}CF_2\text{-}CH_2OCH_2\text{-}P$

where P is the piperonyl endgroup ($\text{-}CH_2\text{-}phenyl{=}O_2{=}CH_2$)

Fomblin ZDOL is synthesized by photo-oxidation of hexafluoropropylene, and consists of linear and random copolymers of two backbones: perfluoromethylene oxide (C_1) and perfluoroethylene oxide (C_2) [16]. Both C_1 and C_2 backbones have acetal units ($\text{-}O\text{-}CF_2\text{-}O$). In addition, ZDOL has two active OH endgroups on each chain end. Demnum is made similarly but starts with 2,2,3,3-tetrafluoro-oxetane; the hydrogen atoms in the resulting polymers are replaced by fluorine atoms by subsequent contact with F_2 [17]. There are no acetal units within Demnum's chemical structure. Demnum SA has only one active OH endgroup and the other is a non-active CF_3 endgroup. AM has the same backbones (C_1 and C_2) as ZDOL. However, AM has two non-active piperonyl endgroups ($-CH_2$-phenyl$=O_2=CH_2$). The molecular weights of the lubricants in our study are 4200, 5500, and 3001, respectively.

III. Results and Discussions

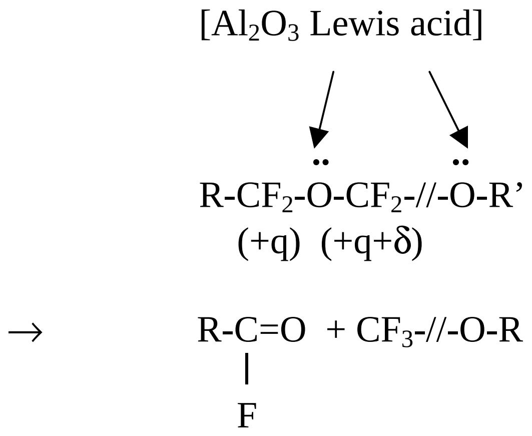
Before starting the friction tests, the background intensities were recorded for 80 seconds by the mass spectrometer. Figure 1 shows the friction coefficient curves for the 12Å ZDOL 4200 lubricated hydrogenated carbon overcoated (CH_X) disks. For the 70Å DLC-coated Al_2O_3/TiC slider, the friction coefficient started at 0.9 and increased steadily to 1.3 within 650 drag cycles. No wear track was observed after 650 drag cycles. For the uncoated Al_2O_3/TiC slider, the friction coefficient increased to a peak value of 6 immediately and dropped to 0.3 after reaching its peak value. A wear track was observed on the disk just after the friction coefficient dropped. The friction variation, as shown in Fig. 1, is most likely due to three-body contact resulting from small wear particles that were generated at the head-disk interface. The above results indicate that 12Å ZDOL 4200 has good lubricating action against the 70Å DLC-coated Al_2O_3/TiC sliders, but little lubricating action against uncoated Al_2O_3/TiC sliders. Figures 2 and 3 show the friction coefficient curves for the 12Å Demnum SA 5500 and AM 3001 lubricants**,** respectively.

Figure 4 shows the integrated mass spectra of the degradation fragments produced at the head-disk interface. The four primary peaks are from the mass fragments CFO (47), CF_2O (66), CF_3 (69), and C_2F_5 (119). In our previous studies of CHx carbon overcoats paired with carbon-coated sliders [13], the primary decomposition mechanism of PFPEs was due to frictional effects, and it was characterized by the generation of CFO (47), and CF_2O (66). The absence of a carbon-coating led to a more complex catalytic decomposition mechanism of PFPEs, and it was characterized by the generation of CF_3 (69) and C_2F_5 (119). In order to eliminate the background effect spectrum the background level was subtracted from the integrated mass spectrum. This mass spectrum for the 70Å DLC coated Al_2O_3/TiC slider is similar to that of PFPE vapor when heated to 300^oC as reported by Kasai et al. [5], where the primary decomposition peaks are masses 47 (CFO) and 66 (CF_2O) due to frictional heating [13].

In Fig. 4 (a) for the DLC coated slider case, more of the AM lubricant was decomposed than ZDOL or Demnum under the same UHV drag condition. One possible explanation is that, without any active OH endgroup bonded strongly to the carbon overcoats, the AM lube experiences a much faster removal rate than ZDOL (two active OH endgroups) or Demnum SA (one active OH endgroup) during the contact sliding. The active OH endgroups of ZDOL or Demnum SA “attach” themselves to active sites on the carbon surface and mitigate the “spin-off” rate during the drag tests. These results indicate that a good lubricant should have at least one very active OH endgroup that provides enough adsorption energy with the disk carbon surface.

The decomposition mechanisms of PFPEs in the case of the uncoated Al_2O_3/TiC slider are much more complicated than those with the DLC coated slider. For the uncoated slider, catalytic reactions control the PFPE decomposition and the catalytic reactions lead to the generation of masses 69 (CF_3) and 119 (C_2F_5). In Fig. 4 (b) for the uncoated slider, the degradation intensities of the catalytic associated fragments CF_3 and C_2F_5 of the ZDOL lube are much greater than those for the Demnum SA or AM lubes. In our previous paper [14] we observed that the catalytic reactions occur at the OH endgroup functionals, where the fluorine atom transfer is from the OH endgroup to the internal sector in the presence of an Al_2O_3 surface. These results indicate that with a non-active endgroup that acts loosely with the Al_2O_3 surface of the uncoated slider, Demnum SA experiences a much reduced rate of catalytic decomposition - the non-active endgroup of the Demnum SA prevents the catalytic decomposition. Li et al. [18] also observed that the presence of Lewis acids sites and reactive OH species are both necessary for the catalytic decomposition of PFPE lubricants. It is believed that the role of the active OH endgroup is to "anchor" the PFPE molecules to the Al_2O_3 surface for further decomposition.

However, according to Kasai [20,21], that Demnum the less catalytic degradation in the presence of the Al_2O_3 surface (Lewis acid) in Demnum is due to the effect of the acetal units. He found that the catalytic degradation of ZDOL occurs most readily at the acetal units within the internal backbones with the following intramolecular disproportionation reaction:



$$\begin{array}{c}[Al_2O_3\ \text{Lewis acid}]\\ \swarrow\qquad\searrow\\ R\text{-}CF_2\text{-}\ddot{O}\text{-}CF_2\text{-//-}\ddot{O}\text{-}R'\\ (+q)\ \ (+q+\delta)\end{array}$$

$$\rightarrow\qquad \underset{\displaystyle F}{\underset{|}{R\text{-}C}}{=}O\ +\ CF_3\text{-//-}O\text{-}R \qquad (1)$$

The reaction (1) occurs when differential charges are induced on the two carbon atoms of an ether linkage by the simultaneous interaction of two successive ether oxygens with Lewis acid sites present at the Al_2O_3 surface [22, 23]. The susceptibility of the various PFPE to this reaction is hence determined by the disposition of the two oxygens flanking the monomer unit, and the net atomic charges of the carbons involved in the fluorine transfer. Therefore, ZDOL performs more catalytic degradation with the uncoated Al_2O_3/TiC sliders than Demnum. The greater vulnerability of ZDOL toward catalytic degradation is due to the presence of acetal units, -O-CF_2-O-, in the polymeric chains. More information about this mechanism could be found in Kasai [23].

Figure 5 shows the wear durability of these disks lubricated with different lubricants. For the DLC coated slider case AM has a poor wear durability, since AM has a faster removal rate because of its very weak adsorption with the disk carbon surface. However, both ZDOL and Demnum SA pass 700 drag cycles without wear. For the uncoated slider case, only Demunm SA shows very good wear durability. Again, the non-acetal backbones and the non-active endgroup of Demnum SA prevents the catalytic decomposition in the presence of the Al_2O_3 surface, resulting in a much better wear performance than ZDOL.

Figure 6 shows the weight loss observed on the Z-lube and D-lube when heated in contact with Al_2O_3 (1 wt. %) at 200^oC. In the actual experiment the degradation was induced by placing a given amount (5 g) of lubricant and 1 wt. % of Al_2O_3 in a test lube, and immersing the tube in an oil bath maintained at a desired temperature (200^oC). For each lubricant, the weight loss was measured after the heat treatment for a given period of time, and the remaining fluid was analyzed by F-19 NMR. In Fig. 6, the weight loss of D-lube is only 0.4% after four hours heating at 200^{o}C, however, the weight loss of Z-lube is 96% after 2 hours heating at the same temperature. These results further support our data from the UHV drag tests that ZDOL lube experiences a much stronger catalytic decomposition than Demnum lube in the presence of the Al_2O_3 surface.

However, Demnum performs very poorly during CSS tests due to its high viscosity. Waltman et al. [24] used quantum chemical modeling calculations to understand how the –CF_2O- (C_1) and -CF_2CF_2O- (C_2) structural units in the ZDOL backbone can influence the bonding kinetics. They observed that the barrier for internal rotation about the C-O bonds in ZDOL will be significantly smaller than those rotation about the C-C bonds. Also, rotations about the C-O bond in the –CF_2O- (C_1) units are more facile than either rotations about the C-C or C-O bonds in the -CF_2CF_2O- (C_2) units, increasing the C_1/C_2 ratio in the ZDOL backbone will increase the relative flexibility of the ZDOL polymer. The rotations about either the C-O or C-C bonds in the Demnum -$CF_2CF_2CF_2O$- units are even more difficult than those within ZDOL's backbones. Therefore, Demnum's mobility is poor as compared to ZDOL, resulting in the higher viscosity and higher stiction in CSS tests.

IV. Conclusions

The experiments presented here illustrate the complex chemical relationships that occur at the head/disk interface during the UHV drag tests. The UHV tribochamber was used to monitor the gaseous wear products generated at the HDI during dragging. The UHV drag tests show that a good lubricant should have one active endgroup and one non-active endgroup. The active one helps lubricants to be adsorbed very well onto the carbon surface and reduce the removal rate of the lubricants during the contact sliding. In the other hand, the non-active one prevents the catalytic decomposition in the presence of the Al_2O_3 surface of the uncoated slider.

The studies also demonstrate that the catalytic degradation process of ZDOL in the presence of Lewis acid occurs most readily at the acetal units ($-O-CF_2-O$) within the internal backbones (CF_2O and CF_2CF_2O) instead of the endgroup functionals. Therefore, Demnum, without any acetal units, performs less catalytic degradation with the uncoated Al_2O_3/TiC sliders as compared to ZDOL.

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CAPTIONS

Fig. 1: friction coefficient of UHV drag test on 12Å ZDOL 4200 lubricated CHx disk.

Fig. 2: friction coefficient of UHV drag tests on 12Å Demnum SA 5500 lubricated CHx disk.

Fig. 3: friction coefficient of UHV drag test on 12Å AM 3001 lubricated CHx disk.

Fig. 4: integrated degradation intensities of four major AM fragments during UHV drag tests on CHx disks lubricated with different lubricants.

Fig. 5: wear durability of CHx disks lubricated with different lubricants during UHV drag tests.

Figure 6: weight loss observed on PFPE’s when heated in contact with Al_2O_3 (1 wt. %) at 200^{o}C.

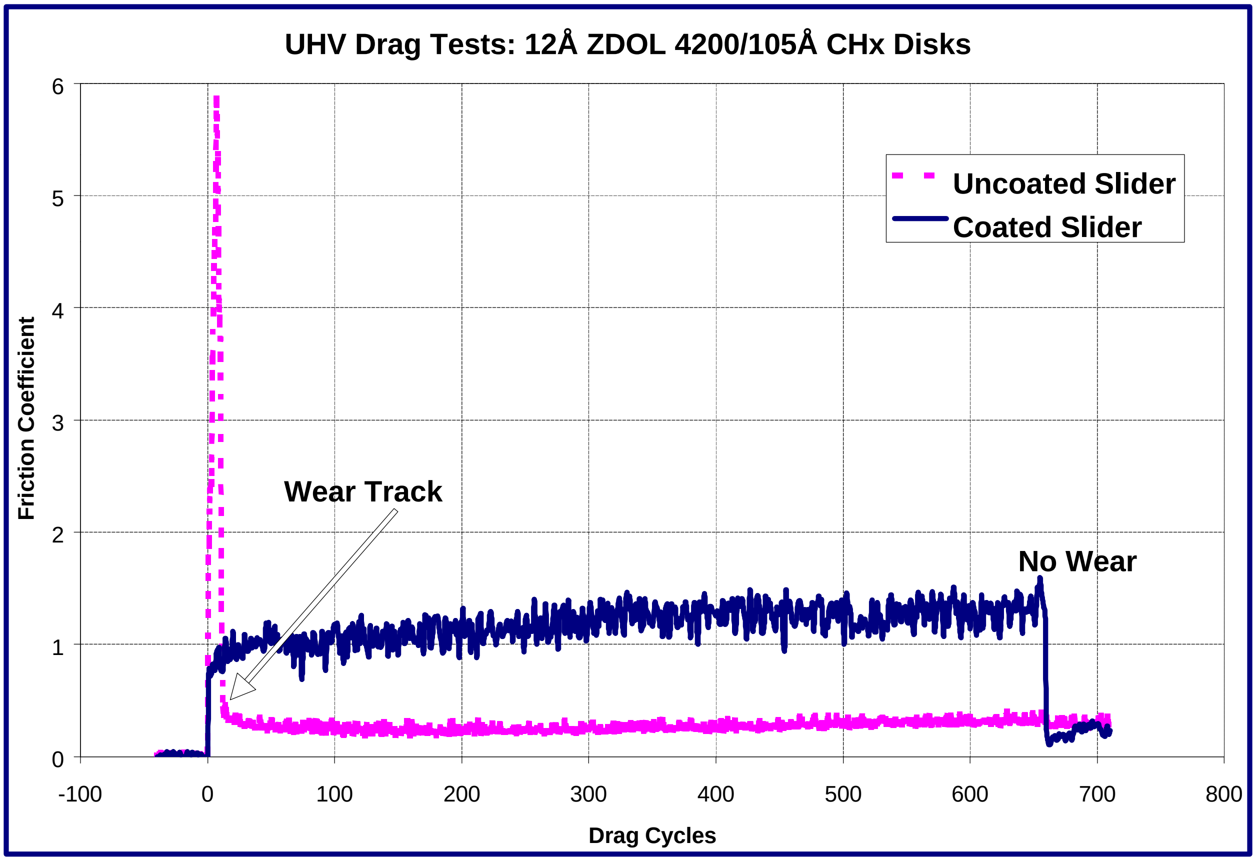

Figure 1: friction coefficient of UHV drag test on 12Å ZDOL 4200 lubricated CHx disk.

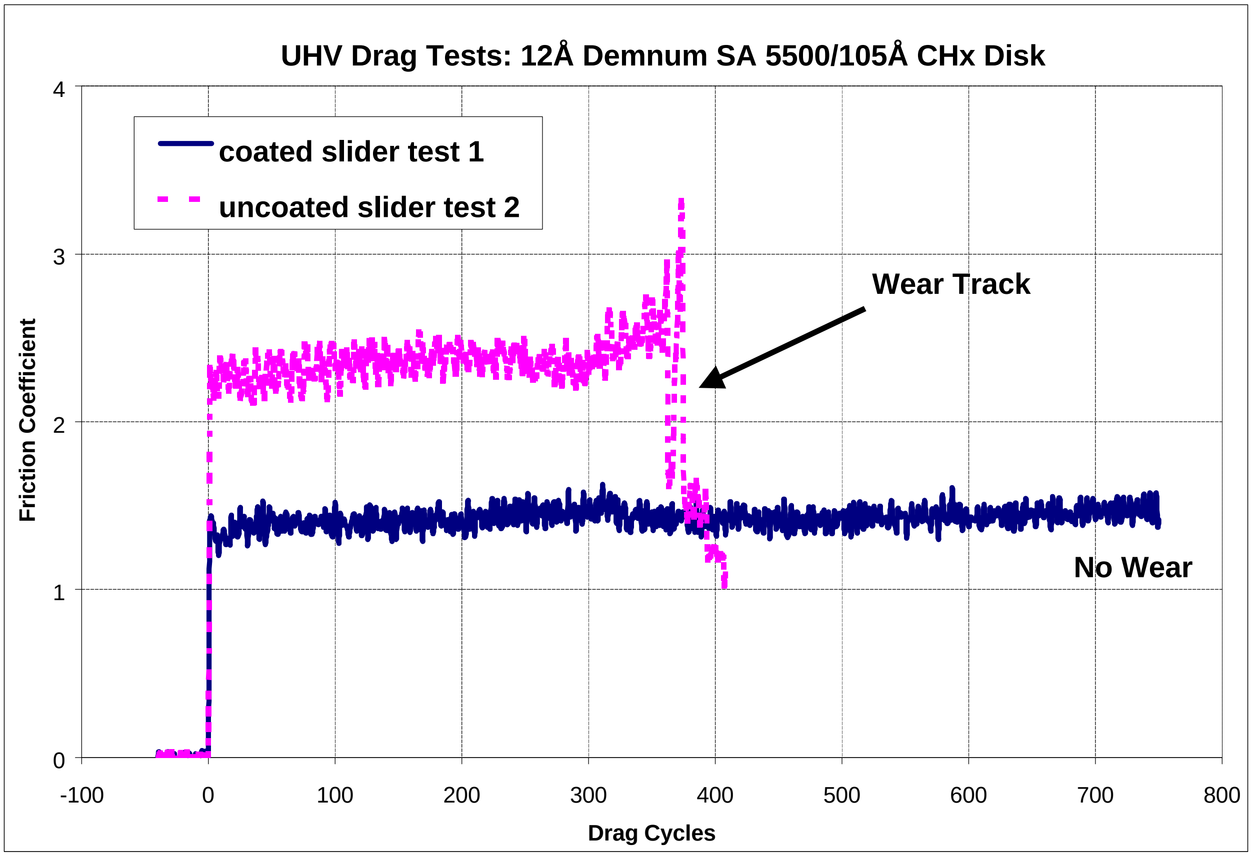

Figure 2: friction coefficient of UHV drag tests on 12Å Demnum SA 5500 lubricated CHx disk.

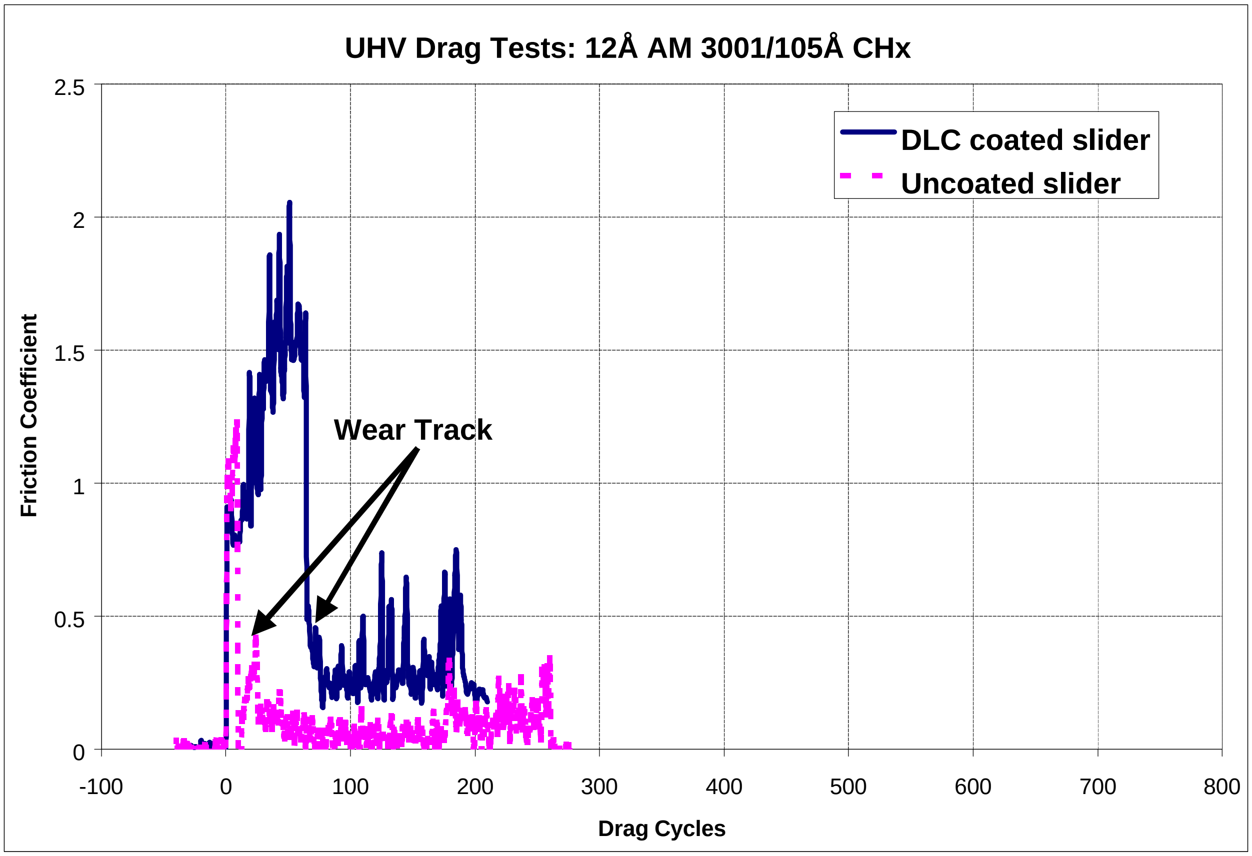

Figure 3: friction coefficient of UHV drag test on 12Å AM 3001 lubricated CHx disk

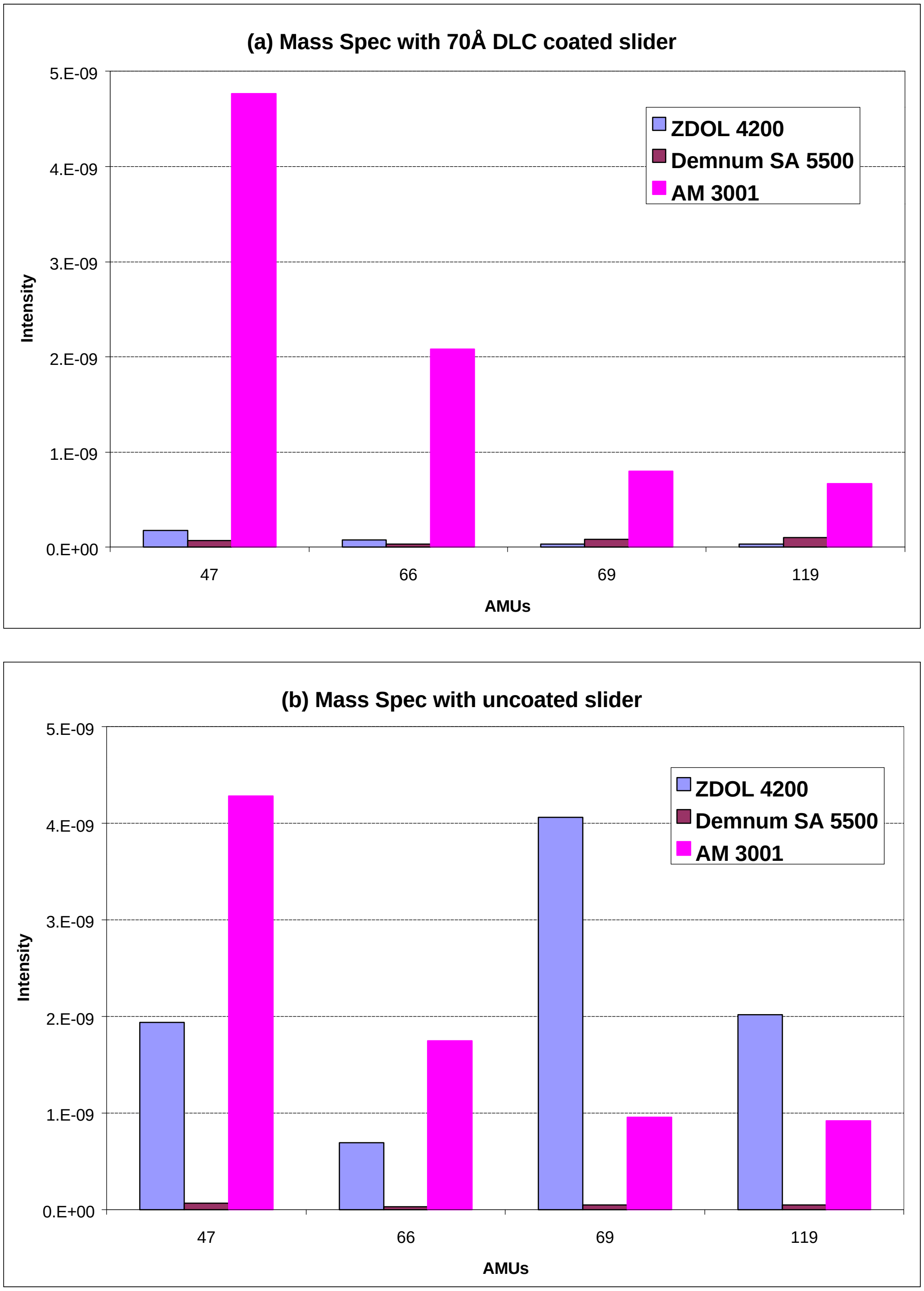

Figure 4: integrated degradation intensities of four major AM fragments during UHV drag tests on CHx disks lubricated with different lubricants: (a) with DLC coated slider; (b) with uncoated slider.

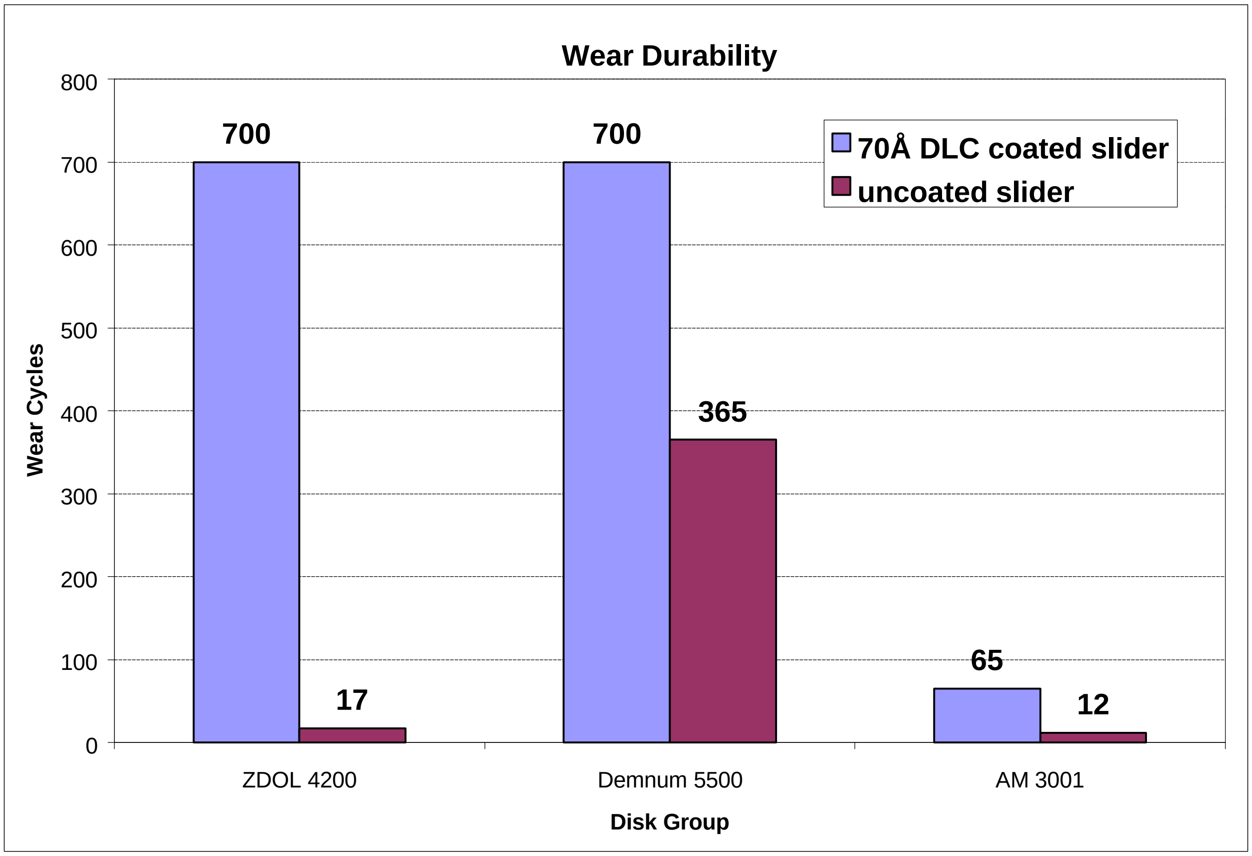

Figure 5: wear durability of CHx disks lubricated with different lubricants during UHV drag tests.

Figure 6: weight loss observed on PFPE's when heated in contact with Al_2O_3 (1 wt. %) at 200°C. (reproduced from Kasai, 1999, with permission).